FURTHER STUDIES OF POLARIZATION CURRENTS DUE TO CHANGE IN ELECTRODE AREA

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Baltimore
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INTRODUCTION

This work was begun with the idea of improving and advancing the experimental technique employed by Glidden (1) in his attempt to examine the mechanism of the adsorption of mercurous ions from solution by a mercury surface. The author desired to compare the results obtained by the galvanometer and the vacuum tube methods which will be described in this paper, following this comparison with an effort at reconciliation between this so-called "electrical method" for the measurement of such adsorption and the "gravimetric method" as used by Seidel (2) and Shea (3).

It will be well at this point to recall some similar studies made previous to this work. The most outstanding of these studies are those of Frumkin (4), Schofield (5), and Heyrovsky (6); other papers will be found in the bibliography of this paper under the notations 7, 8, and 9. The method involved in these studies is that of using the dropping mercury cathode to study electrocapillary phenomena.

As has been observed, the disadvantage of the dropping electrode is the difficulty of interpretation of results due to the following factors:

(1) Rapid formation of the mercury drops in the solution causes changes in the metal ion concentration of the solution in the immediate vicinity of the electrode surface.

(2) Not only do such concentration changes give a distortion of the results in their use for measuring metal ion adsorption, but these concentration changes cause a change of the interfacial tension between the metal and the solution, which change causes a variation in the size of the drops.

(3) Also, if some time is required for the attainment of the adsorption equilibrium and for the orientation of the adsorbed particles on the metal surface, rapid formation of the drops will definitely present an untrue picture of the adsorption mechanism.

This work involves the idea of presenting, very slowly, a mercury surface to the solution, and of measuring very carefully the currents produced.

Until now there has been necessary the assumption that the currents measured are due solely to adsorptive phenomena and not to purely electrostatic forces. We proposed to test this assumption by presenting a mercury surface to a solution of the salt of another metal; if the phenomenon is due to electrostatic forces, a current should be produced; if due to adsorptive forces, no current should be produced.

The description of the work begun with these ideas in mind will follow.

EXPERIMENTAL

Materials. The mercury used in this experiment was purified in the following manner. Mercury secured from the stockroom was put through a pinhole in filter paper twice. After this rough purification, the mercury was rained through a nitric acid column three times, the acid being renewed several times during the purification. To wash out the remaining acid or any mercuric nitrate, the mercury was rained through distilled water twice. Then, for fear some amalgamated metal might be present in the mercury, the mercury was shaken with a mixture of sulfuric acid and potassium permanganate. After this procedure another washing of the mercury in distilled water was carried out. Further attempts at purification involved distilling the mercury twice; the distillation was carried out in a vacuum with a fine stream of air bubbling through the mercury to prevent bumping. In the process of distillation, the first portion of the mercury that distilled over was discarded. The metal was stored in air-tight bottles. During the experiment, care was taken to prevent, as far as possible, grease-film formation on the mercury surfaces.

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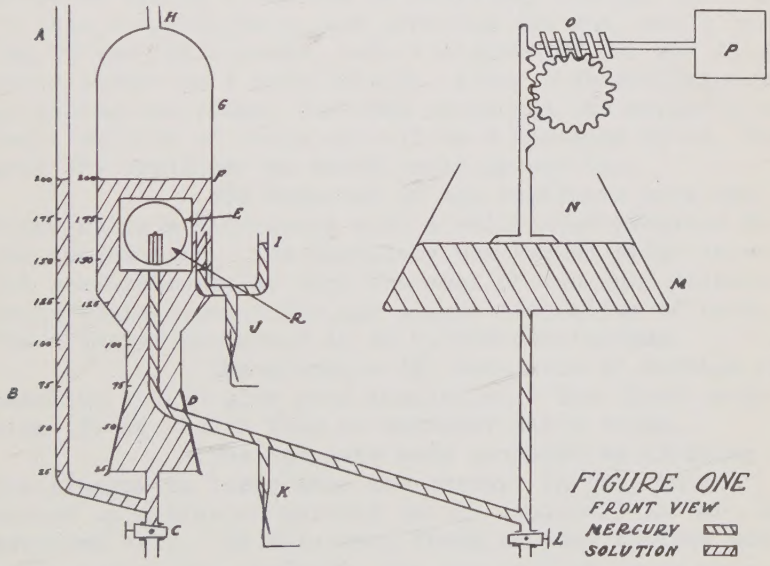
The mercurous sulfate used was that taken from the stockroom. The manufacturer's analysis showed it to contain chlorine, iron, nitric acid, and mercuric sulfate; these impurities, however, were present in such small quantities, most of them in traces, that they gave no trouble.

All water used was carefully de-aerated to eliminate the possibility of the formation of a film of oxide on the mercury electrodes.

The Apparatus and Procedure. The adsorption cell is pictured in Figure One. The opening at (A) was to allow stirring of the solution in the cell after water had been added for dilution; this stirring was accomplished by passing water-pumped, 99.8% pure, nitrogen through a washing train into the cell through (A), where its bubbling through the solution and its leaving the cell at (H) effected the stirring. (B) indicates the calibrations on the side-arm which allowed the removal of definite amounts of the solution from, and accurate



of definite amounts of water to the cell. (C) and (L) indicate stopcocks used for draining the entire apparatus of the solution and of mercury to allow for cleaning between runs. (E) points out a flat window in the cylindrical cell; two such windows were placed opposite each other, so that light passed through the cell to a microscope objective with as little aberration as possible. (F) represents the solution. (J) and (K) show the two copper leads, sealed in Pyrex glass, which led from the mercury electrodes to the galvanometer (or to the amplifier). (R) points out the capillary on which the mercury drop rested. (M) represents a section of the three-liter Erlenmeyer flask which was used to give a large mercury surface. (N) is a plunger, connected to the clock mechanism (P) by the system of gears (O), which dipped into the mercury contained in (M). The purposes of each part of the apparatus will be discussed later, as the various parts of the procedure are brought under consideration.

The capillary mentioned above was prepared by taking a section of capillary tubing, inserting it into a drill-press, and pressing its end, while turning in the drill-press, into a mixture of oil and fine emery powder on a metal plate. After this preliminary polishing was ended, the same procedure was employed using a mixture of rouge and oil on a hardwood block. This gave the capillary an excellently ground tip.

The diameter of the capillary bore was found using a microscope with a calibrated eyepiece for the measurement. The capillary was turned after each of ten measurements, so that the mean of ten such measurements would account for any slight inequality of bore. The diameter was found to be 0.0856 centimeters.

The plungers (N) were made of formica or bakelite rod to give good insulation. The clock mechanism (P) was taken from an ordinary alarm clock.

The currents were produced by allowing the plunger to lower into the mercury in (M), which pushed up a drop of mercury on the capillary in the adsorption cell. In this way, fresh mercury surface was presented to the solution, and the ensuing adsorption created a current which was led from the solution through the electrodes (J) and (K).

Measurement of Area Changes. Two factors were brought into play to overcome the objection of too-rapid drop formation. First, the area of the mercury surface in (M) was made approximately 10,000 times that of the area of the cross-section of the capillary. Hence the volume change of the mercury drop is approximately one ten-thousandth of the volume change in (M). Secondly, the lowering of the plunger was slowed down by placing between the clockwork and the plunger a year-system with a gear-ratio of one hundred to one. The area change of the drop could be varied within limits by increasing or decreasing the size of the plunger. With such an arrangement it was possible to slow up the area change in the drop to a value as low as 4×10^{-7} cm.^{2} per second.

In making measurements of area change, the rate of growth of the drop was followed by means of cross-hairs in the calibrated eyepiece of a microscope. Light for the field was furnished by a 25-watt bulb mounted in a reflector behind the adsorption cell. It should be noted here that the false meniscus presented by a mercury surface in a microscopic field was eliminated by the simple expedient of shading off part of the light.

The actual measurement of the area of the drop was had from obtaining the varying heights of the drop above the capillary as it was made to grow.

This method was arrived at through the following considerations. If r is the radius of a sphere and h the height of a segment of the sphere, the area of the segment of the sphere is $2\pi rh$. The radius of the drop on the capillary tip varies with the height of the drop above the tip. If the drop is spherical, the average rate of change of mercury surface in contact with the solution is found by the method below. If

h_0 = height of meniscus above capillary tip at time 0;
h_1 = height of meniscus above capillary tip at time T seconds;
r_0 = radius of curvature of drop at h_0;
r_1 = radius of curvature of drop at h_1;
S_0 = area of segment of sphere at h_0;
S_1 = area of segment of sphere at h_1;

a = radius of capillary bore;

then,

$$r_0^2 = a^2 + (h_0 - r_0)^2$$

and,

$$r_0 = \frac{a^2 + h_0^2}{2h_0}$$

If a similar expression for r_1 is set up, then, since $S_0 = 2\pi r_0 h_0$ and $S_1 = 2\pi r_1 h_1$,

$$\frac{\Delta S}{\Delta T} = \frac{S_1 - S_0}{T - o} = \frac{2\pi r_1 h - 2\pi r_0 h_0}{T - o} = \frac{\pi(h_1^2 - h_0^2)}{\Delta T}$$

This expression, giving the average rate of change of area over the time interval ΔT, can be used for calculation of instantaneous rate of change if ΔS is made small.

This method was used for the measurements with the vacuum-tube set-up. However, when runs were made using the galvanometer method, the following considerations brought out the idea that better values could be obtained if only Δh were measured instead of actually measuring h_1 and h_0.

If the radius of the drop equals the radius of the capillary, then, in the formula, $\Delta S = 2\pi r \Delta h$, a can be substituted for r, leaving only Δh to measure. It is much easier to measure Δh than actual heights, since such a measurement involved merely focussing twice on the mercury meniscus, whereas measurements of h_1 and h_0 require focussing accurately on the tip of the capillary. This last could not be done without 10%-15% error due to the vague outlines of the capillary tube in the field. If a focus was made on the capillary, the drop passed out of focus. Focussing on the drop involved a maximum error of only 1%. The question is, then, can a be substituted for r? The answer is that such a substitution can be made over a certain range of heights. In Table One is a computation of errors made by this assumption over the height range used in this experiment.

TABLE ONE

h (cm.)	$S = \pi(h_1^2 - h_0^2)$ ($cm.^2$)	$S = 2\pi r \Delta h$ (r=a); ($cm.^2$)	Difference ($cm.^2$)	% Error	
.0825					
.0850	13.20×10^{-4}	13.45×10^{-4}	$.25 \times 10^{-4}$	1.9	
.0860	5.34	5.38	.04	0.7	
.0870	5.34	5.38	.04	0.7	
.0875	13.51	13.45	-.06	0.4	$h_1 = .0875$
					$h_0 = .0850$
.0880	5.34	5.38	.04	0.7	
.0890	5.66	5.38	-.28	4.9	
.0900	13.83	13.45	-.38	2.7	$h_1 = .0900$
					$h_0 = .0875$

Measuring over the entire range, $h_0 = .0850$ cm. to $h_1 = .0900$ cm., we have $\Delta S_2 = \pi(h_1^2 - h_0^2) = 28.27 \times 10^{-4}$ $cm.^2$ and $\Delta S = 2\pi r \Delta h = 26.89 \times 10^{-4}$ $cm.^2$, involving an error of 4.88%. Since this is only slightly above experimental error (2%-3%), it is obviously better to use this method than that of measuring actual heights, where an error of at least 10%-15% is involved. Here, all that had to be done was to read the eyepiece calibrations at approximately $h_1 = .0900$ and $h_0 = .0850$. At these heights the mercury is well out of the capillary, without being high enough for the drop to flatten out.

The Solution. A saturated solution of mercurous sulfate was prepared by allowing an excess of the mercurous sulfate mentioned under Materials to stand in contact with distilled water for six weeks. During this time the solution was subjected to irtermittent shakings daily. A little pure mercury was put in contact with the solution to prevent the formation of the mercuric salt.

After runs had been made using the concentrated solution, other runs were made with the solution in progressive stages of dilution.

Care was taken to prevent, as far as possible, the presence of dissolved oxygen in the solution.

After the solution, made up as above, had been introduced into the cell, 99.8% pure, water-pumped nitrogen was passed through a pyrogallol washing train and through the solution for about twenty-four hours. In subsequent dilutions, the water used was carefully de-aerated before it was added to the solution.

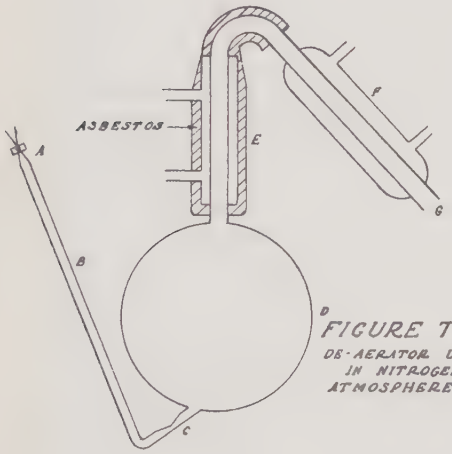


FIGURE TWO
DE-AERATOR USED IN NITROGEN ATMOSPHERE

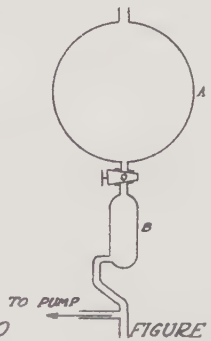


FIGURE THREE
DE-AERATOR USED WITH VACUUM PUMP

This de-aeration was carried out, at various times, in two ways. Figure Two shows the type of apparatus used in the de-aeration process designed by Urry and Paneth (10). Use of this apparatus necessitated slight modifications in the apparatus shown in Figure One to allow the adsorption cell to be evacuated. With these simple modifications, then, the tube (C) in Figure Two was joined to the tube (H) in Figure One. Distilled water, after boiling and sudden cooling without stirring, was placed in the bulb (A). The cell being evacuated, the stopcock between (A) and (B) was slightly cracked, allowing a slow trickle of water from (A). As the water entering (B) was almost instantaneously vaporized, practically all dissolved gases were pulled out. The remaining water vapor condenzed and ran into the adsorption cell. The tube leading to the pump was opened about half a minute in each five minutes to allow the pump to

draw off air removed from the water. According to Urry and Paneth, this operation gives 150 cc. of de-aerated water per hour, containing not more than 10^{-5} cc. of oxygen per 100 cc. of water. With the adsorption cell graduated for volume measurements, the solution could be diluted by drawing off a portion of solution at (C) in Figure One, and by adding water at (H) in Figure One.

The second method was used, not when a vacuum was maintained in the adsorption cell, but when an atmosphere of nitrogen, purified as above, was kept in the cell. The de-aerator used with this outfit is shown in Figure Three. The tube (G) in Figure Three was connected to (H) in Figure One. Distilled water was introduced into the bulb (D) through the gum-rubber tubing (A) connected to (D) by the glass tube (B). After the water was put into the bulb, (A) was connected to the tube bringing in nitrogen. The constriction (C) in the tube (B) caused the nitrogen stream to break up into fine bubbles. This nitrogen stream tended to sweep out any oxygen present. Meanwhile, heat was applied to the water in bulb (D), and water was put through the jacket of the condenser (E). The water in (D) was allowed to reflux, with nitrogen bubbling through, for periods ranging from thirteen to twenty hours. The nitrogen was allowed to escape through an opening between (G, Figure Three) and (H, Figure One). After this reflux period, the rubber tube (A) was shut off with a screw-clamp, and the opening between (G, Figure Three) and (H, Figure One) was closed. The flow of water in the jacket of condenser (E) was stopped, and water was put through the jacket of the condenser (F). Asbestos packed around (E) kept the water from condensing there once the condenser tube warmed up, and the de-aerated water was distilled over into the adsorption cell. Much expansion was taken up in the side-arm (B, Figure One); however, if too great a pressure was built up, the compressed water vapor was allowed to blow off by effecting the momentary opening of the tube between (G, Figure Three) and (H, Figure One). This blowing out of the water vapor, while relieving the pressure, was strong enough to keep air from diffusing into the cell. By this means also, then, the solution was diluted with air-free water.

It was necessary, of course, to know the initial concentration of the solution in order to

calculate the concentrations at various dilutions. A portion of the original solution was analyzed by the electrolytic method given by Treadwell and Hall (11). The analysis showed a mercury content of 0.451 grams of mercury per liter of solution. This corresponds to a mercurous sulfate concentration of 1.12 milli-mols per liter. This value is slightly under the value given for a completely saturated solution of mercurous sulfate. After each dilution, the solution was stirred with purified nitrogen passed in through (A, Figure One).

Current Measurements. The currents produced when the mercury drop was raised into the solution were measured in one of two ways.

At first it was thought that the currents would be so small that a strong amplification would be needed. With this in view, an FP-54 Pliotron tube was secured and set up. This tube was first described in 1930 by Metcalf and Thompson (12) of the General Electric Laboratories. Its characteristics and instructions for its use can be found in Bulletins GET-249A (Circuits for FP-54 Pliotron) and GEJ-246A (Instructions for FP-54 Pliotron); these bulletins are printed by the General Electric Company of New York. Suffice it to say here that the F(-54 Pliotron is a four element thermionic tube, the fourth element serving as a "space-charge" grid to keep down currents due to soft positive rays coming from the filament. The advantages of the tube over other vacuum tubes are, chiefly, (1) that it has a very high grid resistance of the order of 10^{16} ohms instead of 10^{8} or 10^{9} ohms as in most tubes; this high grid resistance is absolutely necessary for the measurement of very small currents; and (2) that it operates at a plate potential of only six volts. This latter fact allows the use of a large capacity storage battery for voltage supply, reducing galvanometer fluctuations, and allowing the use of a more sensitive galvanometer. This factor counteracts the fact that the mutual conductance of the tube is slightly lower than that of ordinary tubes. The normal operating conditions of the tube are:

Filament Voltage	2.5 volts
Filament Current	0.11 amps.
Space Charge Grid	+4.0 volts
Control Grid	-4.0 volts
Plate	+6.9 volts

Under these conditions the tubes have the following average characteristics:

Grid input resistance	10^{16} ohms (app.)
Control grid current	10^{-15} amp. (app.)
Mutual conductance	25 micro-amp./volt
Plate current	40 micro-amp.
Plate resistance	40,000 ohms
Voltage amplification factor	1
Grid capacity	3μμF

A discussion of the theory of amplification with vacuum tubes is given by Rasmussen (13) and by Metcalf and Thompson (12). The latter paper contains a review of some circuits used with the tube. Many others have described circuits, among them being Bennett (14), Dearle and Mathewson (15), Razek and Mulder (16), Nelson (17), Wold (18), Wynn-Williams (19), Eglin (20), Forbinder (21), Brentano (22), Partridge (23), Stadie (24), Hill (25), and DuBridge (26). This list includes some circuits for ordinary three-element thermionic tubes, but they may be adapted for use with the FP-54 Pliotron by providing an extra tap in the plate battery for the inner, or space-charge, grid.

It is obvious that the sensitivity of any d.c. amplifying circuit using FP-54 Pliotron tubes is limited by the stability which may be obtained. In single tube circuits, one of which was used in this work, it is necessary to eliminate drift and fluctuations. The most important causes of drift are (1) slow changes in battery e.m.f., (2) changes in the circuit resistance because of temperature change, and (3) slow changes in the characteristics of the tube. Important sources of fluctuation are (a) improper shielding, (b) poor rheostat contacts, (c) mechanical vibrations, and (d) changes in the emission of the thoriated tungsten filament. (2), (a), (b), and (c) were easily eliminated by careful design and mounting of the apparatus.

The balanced circuit described by W. Soller (27) was selected, at the time of this work, as the best available. A slight modification of this circuit was the one actually used. A diagram of the circuit used is shown in Figure Four. It is seen at once that the

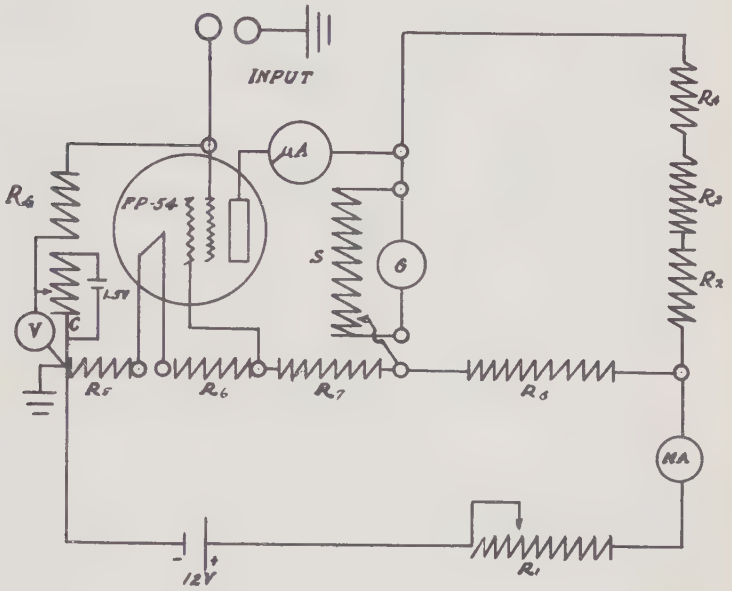


FIG. 4
DIAGRAM OF CIRCUIT USED FOR FP-54 AMPLIFIER

R_1 = 40 ohm POTENTIOMETER

R_2 = 500 " "

R_3 = 20,000 ohm "

R_4 = 20,000 " "

R_5 = 40 ohm RESISTOR

R_6 = 14 " "

R_7 = 18 " "

R_8 = 20 ohm RESISTOR

R_g = 10^7-10^{10} "

S = 10,000 ohm "

G = SENSITIVE GALVANOMETER

V = MILLIVOLTMETER (200 m.v.)

MA = MILLIAMMETER

A = MICROAMMETER

advantage of such a circuit is the conquering of (1), fluctuations due to changes in battery e.m.f. Lately the description of a circuit designed to overcome (d), fluctuations due to changes in filament emission, has been published by Du Bridge and Brown (28).

The requirement for balancing a single tube with the Soller circuit is that a portion of the filament current-plate current curve must be straight. The length of the straight portion determines the range of external fluctuations that can be balanced. This requirement is usually fulfilled for normal operating conditions. With our tube, this portion of the curve lay between the values 20-40 micro-amperes for plate current and 96-100 milli-amperes for filament current. The micro-ammeter and the milli-ammeter (Figure Four), respectively, were used for these readings.

The method of balancing the circuit in preparation for use was as follows:

The galvanometer was brought to zero by adjusting S. The filament current was changed by changing R_1; I_f was changed in this manner until a value of I_f was found at which the galvanometer deflection was a minimum. Now R_2 and R_3 were adjusted so as to make I_f, at the minimum deflection, equal to the rated filament current. At this point the circuit was neutralized and ready for use.

The sensitivity of the amplifier was found by impressing upon the control grid a known potential from a dry-cell connected to the potentiometer (C). This potential could be varied, allowing calibration over the complete range of the galvanometer scale. The potentials were read on the milli-voltmeter (V). After calibration the dry-cell and (C) were removed from the circuit simply by moving the slider on (C) so as to connect directly to R_5.

High Resistances. The resistances (R_g) used for the grid leak were manufactured by the S. S. White Dental Company; they were composition grid leak resistors. Such resistors may be obtained that have values as high as 10^{14} ohms. Resistances of one thousand megohms can be made by ruling India ink marks on drawing paper, hard rubber, or amber, or by sputtering thin metal films onto a glass or quartz rod. However, if an

input resistance of greater than 10^9 ohms is used, fluctuations may be introduced because of the great difficulty of shielding the grid circuit from high frequency disturbances. Grid resistances greater than 10^{11} ohms cannot be used without greatly increasing the time constant of the circuit (29).

The input resistances used in this work were 5.13×10^{10} ohms, 1.22×10^{10} ohms, and 5.5×10^8 ohms. These values were checked from time to time by measuring the rate of leak of the charge on a group of condensers through the resistance to earth. This measurement was made using a Lindemann electrometer. The method was that employed by Glidden (1), and a description of the electrometer and its uses has been made by A. F. and F. A. Lindemann with T. C. Keeley (30).

Fluctuations due to the use of input resistances higher than 10^9 ohms were reduced almost to nothing by making the grid lead as short as possible, insulating it with quartz, and by carefully shielding the entire set-up.

Let it be said here that the entire glass apparatus was suspended on bakelite rods and set on a base of sheet-cork, which base was placed on rubber. The electrical set-up was also carefully insulated. Both glass and electrical units were shielded completely. Precautions were taken to insure complete dryness, good contacts, and well-charged batteries. Potentiometers, resistors, batteries, and galvanometer were all of good quality.

The Second Method of Measuring Currents. For reasons which will be discussed later, it was believed that the total current generated in the adsorption cell was not going through the vacuum tube circuit. It was decided to run the two leads (J) and (K) in Figure One directly to a galvanometer.

A Leeds and Northrup Type HS galvanometer was mounted on picein blocks which rested on a heavy oak stand mounted in concrete. The whole stand, concrete and all, was given a three-point mounting on large rubber stoppers. This almost completely eliminated mechanical vibration. The leads to the galvanometer were cotton-insulated copper wire covered with a layer of paraffin, and were suspended on paraffin blocks.

The galvanometer was calibrated after the method of Harnell and Livingood (31). Two galvanometers with slightly different characteristics were used to double-check the measurements.

Where the tube was capable of measuring currents as small as 1×10^{-14} amperes, the galvanometers were sensitive to 1×10^{-10} amperes.

Summary of the Experimental Procedure. With the apparatus set up as described in the preceding pages, the following procedure was carried out. The clock mechanism was set in operation, lowering the plunger into the mercury reservoir. When the formula, $\Delta S = \pi(h_1^2 - h_0^2)$ was used, measurements were begun as soon as the mercury had reached a reasonable height (0.02 - 0.03 cm.) above the capillary tip. The tube circuit having been balanced up, the cell was connected into the circuit by means of a switch, h_0 was recorded, and the galvanometer deflection noted. At regular 300 second intervals (by a stop watch) thereafter, the height of the drop and the galvanometer deflection were recorded. This was continued until the tube circuit showed fluctuations, indicating overbalance due to some of the causes mentioned above. This completed one run.

It so happened that the galvanometer alone was used when the formula $\Delta S = 2\pi r \Delta h$ was used. In this method, the cross-hair of the micrometer eyepiece was set at approximately 0.085 cm. above the capillary tip. The clockwork was started, lowering the plunger into the reservoir of mercury. The drop was allowed to grow until its edge just touched the cross-hair in the eyepiece. The galvanometer was then connected to the cell by the closing of a switch. The cross-hair was moved up a distance of 0.005 cm. The time required for the drop to grow from the initial to the final height was recorded on a stop watch. The galvanometer deflection was read at sixty-second intervals during this time, and the average deflection was used to calculate the current generated.

Several runs were made at each concentration of the solution used, the mean of these runs being used as the true value.

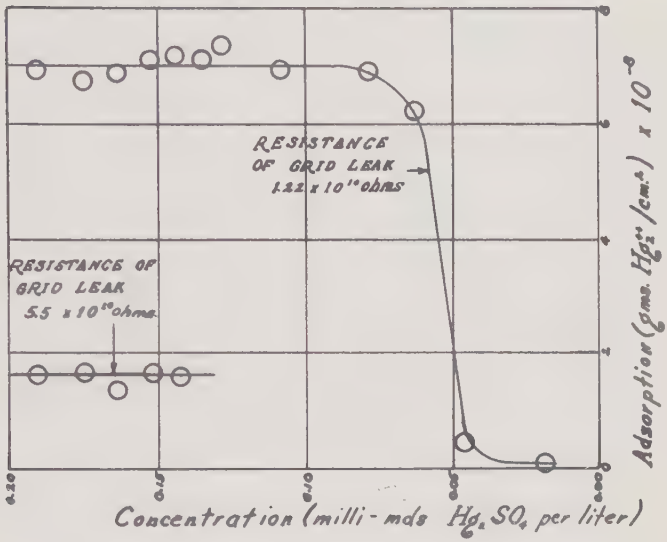

RESISTANCE OF GRID LEAK 1.22 x 10^14 ohms
RESISTANCE OF GRID LEAK 5.5 x 10^13 ohms.
Adsorption (gms. Hg2++/cm.2) x 10^-9
Concentration (milli-mols Hg2SO4 per liter)

FIGURE 5

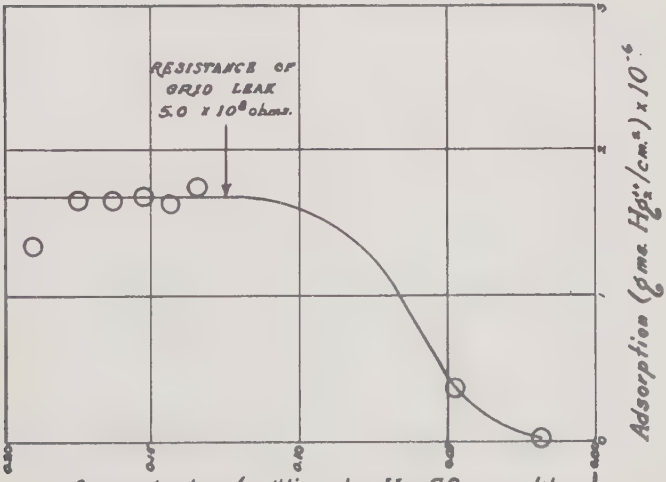
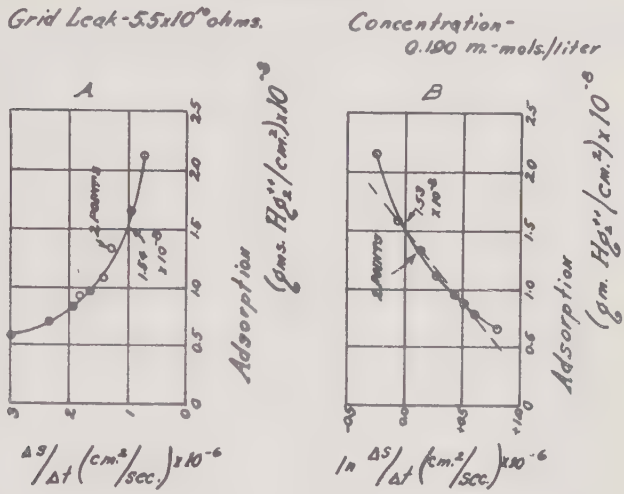


FIGURE 6

FIGURE 7



EXPERIMENTAL RESULTS

The tables immediately following this paragraph give the results obtained using the FP-54 Pliotron. The concentration in milli-mols of mercurous sulfate per liter, and the value of the grid leak are noted at the top of each table. Each horizontal line represents a run. The column at the left gives the average rate of area change of mercury surface in contact with the solution, the second column gives the current in amperes flowing between the electrodes in the cell, the third column gives the adsorption per second (calculated by multiplying the current by the factor 2.07×10^{-3} grams of mercurous ion per coulomb), and the fourth column gives the adsorption per unit surface, expressed in grams of mercurous ion per square centimeter of mercury surface. The latter values were found by simply dividing the adsorption per second by the rate of change of mercury surface.

TABLE TWO

Concentration of solution = 0.190 milli-mols per liter
Grid leak = 5.13×10^{10} ohms

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
3.03×10^{-6}	7.43×10^{-12}	1.54×10^{-14}	5.08×10^{-9}
1.90	7.43	1.54	8.11
1.57	7.46	1.54	9.81
1.36	7.50	1.55	11.40
2.30	7.52	1.56	6.78
1.15	7.55	1.56	13.57
0.73	7.56	1.56	21.37
0.94	7.58	1.57	16.70
1.15	7.59	1.57	13.65
1.78	7.64	1.58	8.88

TABLE THREE

Concentration of solution = 0.175
Grid leak = 5.13×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
1.05×10^{-6}	7.52×10^{-12}	1.56×10^{-14}	14.86×10^{-9}
0.73	7.54	1.56	21.37
1.58	7.46	1.54	9.75
2.10	7.50	1.55	7.38
0.73	7.52	1.56	21.37

TABLE FOUR

Concentration of solution = 0.163
Grid leak = 5.13×10^{10}

$\frac{\Delta S}{\Delta T}$	Current	Adsorption	Adsorption
($cm.^2/sec.$)	(amps.)	(gms./sec.)	(gms. $Hg_2^{++}/cm.^2$)
1.47×10^{-6}	7.10×10^{-12}	1.47×10^{-14}	10.00×10^{-9}
3.35	7.09	1.47	4.39
2.62	7.07	1.46	5.57
3.99	7.06	1.46	3.68
3.35	7.06	1.46	4.36
5.08	7.10	1.47	2.89
4.40	7.10	1.47	3.34
3.48	7.76	1.60	4.60
3.10	7.78	1.61	5.19
6.80	7.77	1.61	2.37
6.43	7.81	1.62	2.52
3.20	7.23	1.50	4.69
6.68	7.31	1.52	2.28
7.11	7.37	1.52	2.14
6.26	7.31	1.52	2.43
6.80	7.31	1.52	2.24
5.75	7.31	1.52	2.64
4.20	7.30	1.51	3.60
5.55	7.31	1.52	2.74
6.50	7.66	1.59	2.45

TABLE FIVE

Concentration of solution = 0.152
Grid leak = 5.13×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
3.23×10^{-6}	7.60×10^{-12}	1.57×10^{-14}	4.90×10^{-9}
2.51	7.61	1.58	6.30
1.99	7.61	1.58	7.90
1.57	7.62	1.58	10.10
2.05	7.63	1.58	7.70
1.47	7.65	1.58	10.70
1.19	7.65	1.58	13.20
0.55	7.66	1.59	29.20
0.45	7.68	1.59	35.30
0.67	7.70	1.59	23.70
0.80	7.70	1.59	20.00
0.81	7.70	1.59	19.70

TABLE SIX

Concentration of solution = 0.143
Grid leak = 5.13×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
2.26×10^{-6}	7.55×10^{-12}	1.56×10^{-14}	6.90×10^{-9}
1.30	7.56	1.56	12.00
1.32	7.61	1.58	12.00
1.15	7.63	1.58	13.70
0.93	7.64	1.58	17.00
1.36	7.65	1.58	11.60
1.89	7.65	1.58	17.80
0.76	7.65	1.58	20.80
1.24	7.66	1.59	12.80
1.10	7.66	1.59	14.50

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TABLE SIX (Con't.)

0.47×10^{-6}	7.66×10^{-12}	1.59×10^{-14}	23.80×10^{-9}
1.27	7.66	1.59	12.50
0.96	7.67	1.59	16.60
0.97	7.63	1.58	16.30
2.12	7.65	1.58	7.50

(Note change of grid leak in the following tables.)

TABLE SEVEN

Concentration of solution = 0.190
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
4.55×10^{-6}	3.32×10^{-11}	6.87×10^{-14}	1.51×10^{-8}
1.10	3.34	6.87	6.25
0.52	3.36	6.96	13.28
0.73	3.35	6.93	9.49
0.83	3.35	6.93	8.35
1.04	3.35	6.93	6.66
0.73	3.35	6.93	9.49
0.83	3.35	6.93	8.35
0.83	3.35	6.93	8.35
0.73	3.35	6.93	9.49
1.05	3.35	6.93	6.64
0.73	3.10	6.42	8.79
0.73	3.10	6.42	8.79
0.83	3.11	6.44	7.76
0.83	3.12	6.46	7.78
0.83	3.12	6.46	7.78
0.94	3.13	6.48	6.89
0.63	3.18	6.58	10.44
1.05	3.15	6.52	6.21

TABLE EIGHT

Concentration of solution = 0.175
Grid leak = 1.22×10^{10}

$\frac{\triangle S}{\triangle T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
2.50×10^{-6}	3.25×10^{-11}	6.73×10^{-14}	2.69×10^{-8}
0.94	3.26	6.75	7.18
1.25	3.27	6.77	5.42
1.15	3.28	6.80	5.91
2.10	3.29	6.81	3.24
1.36	3.30	6.83	5.02
0.63	3.31	6.85	10.87
1.46	3.32	6.87	4.71
0.63	3.33	6.89	10.94
1.46	3.33	6.89	4.72
1.15	3.34	6.91	6.01
1.46	3.35	6.93	4.75

TABLE NINE

Concentration of solution = 0.163
Grid leak = 1.22×10^{10}

$\frac{\triangle S}{\triangle T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
2.32×10^{-6}	3.31×10^{-11}	6.85×10^{-14}	2.95×10^{-8}
2.68	3.31	6.85	2.56
2.11	3.33	6.89	3.27
1.48	3.33	6.89	4.66
2.34	3.31	6.85	2.93
1.44	3.31	6.85	4.76
1.93	3.33	6.89	3.57
1.56	3.35	6.93	4.44
1.41	3.36	6.96	4.94
0.83	3.37	6.98	8.41

TABLE TEN

Concentration of solution = 0.152
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
1.87×10^{-6}	3.42×10^{-11}	7.08×10^{-14}	3.79×10^{-8}
1.51	3.43	7.10	4.70
1.43	3.41	7.06	4.94
1.99	3.41	7.06	3.55
1.14	3.41	7.06	6.19
0.78	3.41	7.06	9.05
0.78	3.39	7.02	9.00
1.06	3.41	7.06	6.66
1.73	3.41	7.06	4.08
0.68	3.41	7.06	10.38
0.41	3.48	7.20	17.56
0.54	3.48	7.20	13.33
0.69	3.47	7.18	10.41
0.28	3.47	7.18	25.64
0.55	3.46	7.16	13.02
0.70	3.47	7.18	10.26
0.57	3.44	7.12	12.49
1.00	3.44	7.12	7.12
1.01	3.44	7.12	7.05

TABLE ELEVEN

Concentration of solution = 0.143
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
1.07×10^{-6}	3.45×10^{-11}	7.14×10^{-14}	6.67×10^{-8}
1.18	3.47	7.18	6.08
0.94	3.48	7.20	7.66

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TABLE ELEVEN (Con't.)

1.06×10^{-6}	3.49×10^{-11}	7.22×10^{-14}	6.81×10^{-8}
0.59	3.50	7.25	12.29
1.19	3.51	7.27	6.11
0.61	3.51	7.27	11.92
0.93	3.51	7.27	7.82
1.27	3.51	7.27	5.72
0.64	3.51	7.27	11.36
0.65	3.51	7.27	11.18
0.44	3.51	7.27	16.52
0.50	3.57	7.39	14.78
0.34	3.58	7.41	21.79
0.40	3.58	7.41	18.53
0.29	3.47	7.18	24.76

TABLE TWELVE

Concentration of solution = 0.134
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$	Current	Adsorption	Adsorption
(cm.^{2}/sec.)	(amps.)	(gms./sec.)	(gms. Hg_2^{++}/cm.^{2})
0.59×10^{-6}	3.36×10^{-11}	6.96×10^{-14}	11.80×10^{-8}
0.68	3.36	6.96	10.24
0.90	3.36	6.96	7.73
0.92	3.37	6.98	7.59
0.62	3.37	6.98	11.26
1.37	3.37	6.98	5.09
0.75	3.37	6.98	9.31
0.65	3.36	6.96	10.71
1.33	3.36	6.96	5.23
1.13	3.36	6.96	6.16
1.27	3.35	6.93	5.46
1.18	3.32	6.87	5.82
1.19	3.32	6.87	5.77
1.71	3.34	6.91	4.04
1.12	3.35	6.93	6.19
1.14	3.33	6.89	6.04

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TABLE TWELVE (Con't.)

0.89×10^{-6}	3.35×10^{-11}	6.93×10^{-14}	7.79×10^{-8}
0.25	3.33	6.89	27.56
1.19	3.30	6.83	5.74
1.43	3.28	6.79	4.75
1.77	3.27	6.77	3.82

TABLE THIRTEEN

Concentration of solution = 0.127
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$	Current	Adsorption	Adsorption
($cm.^2$/sec.)	(amps.)	(gms./sec.)	(gms. $Hg_2^{++}/cm.^2$)
2.73×10^{-6}	3.41×10^{-11}	7.06×10^{-14}	2.59×10^{-8}
0.67	3.42	7.08	10.57
0.82	3.41	7.06	8.61
0.57	3.41	7.06	12.39
0.52	3.41	7.06	13.58

TABLE FOURTEEN

Concentration of solution = 0.107
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$	Current	Adsorption	Adsorption
($cm.^2$/sec.)	(amps.)	(gms./sec.)	(gms. $Hg_2^{++}/cm.^2$)
6.56×10^{-6}	3.18×10^{-11}	6.58×10^{-14}	1.00×10^{-8}
2.44	3.18	6.58	2.70
3.18	3.17	6.56	2.06
1.99	3.17	6.56	3.30
2.92	3.19	6.60	2.26
3.17	3.27	6.77	2.14
1.51	3.28	6.79	4.50

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TABLE FOURTEEN (Con't.)

3.27×10^{-6}	3.24×10^{-11}	6.71×10^{-14}	2.05×10^{-8}
1.36	3.29	6.81	5.01
1.76	3.30	6.83	3.88
2.18	3.28	6.79	3.11
1.00	3.36	6.96	6.96
1.61	3.37	6.98	4.34
1.02	3.37	6.98	6.84
1.02	3.37	6.98	6.84
1.02	3.41	7.06	6.88
0.21	3.41	7.06	33.62

TABLE FIFTEEN

Concentration of solution = 0.080
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
0.58×10^{-6}	3.48×10^{-11}	7.20×10^{-14}	12.41×10^{-8}
1.66	3.35	6.93	4.17
1.32	3.39	7.02	5.32
0.65	3.38	7.00	10.77
1.16	3.38	7.00	6.03
1.17	3.37	6.98	5.97
1.03	3.35	6.93	6.73
0.78	3.30	6.83	8.76
1.56	3.36	6.96	4.46
0.74	3.19	6.60	8.92
0.59	3.19	6.60	11.19
0.51	3.19	6.60	12.94
0.71	3.18	6.58	9.27
0.70	3.18	6.58	9.31
0.84	3.18	6.58	7.83

TABLE SIXTEEN

Concentration of solution = 0.064
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
0.71×10^{-6}	3.05×10^{-11}	6.31×10^{-14}	8.89×10^{-8}
0.73	3.03	6.27	8.59
0.90	3.02	6.25	6.95
0.61	2.98	6.17	10.12
0.87	2.97	6.15	7.07
0.73	2.95	6.11	8.37
0.66	2.93	6.07	9.20
0.42	2.92	6.04	14.38
0.43	3.00	6.21	14.44
0.25	2.98	6.17	24.68
0.44	2.97	6.15	13.98
0.52	2.98	6.17	11.87
0.43	3.00	6.21	14.44

TABLE SEVENTEEN

Concentration of solution = 0.048
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.^{2})
0.48×10^{-6}	2.47×10^{-12}	5.11×10^{-15}	10.65×10^{-9}
0.77	2.14	4.43	5.75
1.19	2.12	4.39	3.69
1.00	2.12	4.39	4.39
0.72	2.13	4.41	6.13
0.89	2.11	4.37	4.91
0.90	2.14	4.43	4.92
0.98	2.16	4.47	4.56

TABLE EIGHTEEN

Concentration of solution = 0.018
Grid leak = 1.22×10^{10}

$\frac{\Delta S}{\Delta T}$	Current	Adsorption	Adsorption
($cm.^2/sec.$)	(amps.)	(gms./sec.)	(gms. $Hg_2^{++}/cm.^2$)
1.43×10^{-6}	3.62×10^{-13}	7.49×10^{-16}	5.24×10^{-10}
1.70	3.32	6.67	3.92
1.39	3.32	6.67	4.80
0.71	3.82	7.91	11.14
1.79	4.52	9.36	5.23
1.35	4.02	8.32	6.16
1.11	5.63	11.65	10.50
1.14	3.62	7.49	6.57

TABLE NINETEEN (NOTE CHANGE OF GRID LEAK)

Concentration of solution = 0.190
Grid leak = 5×10^8 ohms

$\frac{\Delta S}{\Delta T}$	Current	Adsorption	Adsorption
($cm.^2/sec.$)	(amps.)	(gms./sec.)	(gms. $Hg_2^{++}/cm.^2$)
1.36×10^{-6}	6.75×10^{-10}	1.40×10^{-12}	1.03×10^{-6}
0.90	6.80	1.41	1.57
0.61	4.51	0.93	1.52
0.63	6.05	1.25	1.98
0.67	7.59	1.57	2.35
2.18	1.54	0.32	0.15
1.29	1.12	0.23	0.18
0.73	5.23	1.08	1.48
2.50	6.97	1.44	0.58
3.24	1.03	0.21	0.07
1.47	1.95	0.40	0.23
1.88	3.49	0.72	0.38
3.56	6.77	1.40	0.39

TABLE TWENTY

Concentration of solution = 0.175
Grid leak = 5×10^8

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
4.07×10^{-6}	7.00×10^{-10}	1.45×10^{-12}	0.36×10^{-6}
2.07	6.98	1.44	0.70
3.24	7.09	1.47	0.45
3.45	7.29	1.51	0.44
1.67	7.47	1.55	0.93
2.62	7.66	1.59	0.61
1.47	7.78	1.61	1.10
1.26	7.80	1.61	1.28
1.05	8.06	1.67	1.59
1.15	6.98	1.44	1.25
1.88	7.77	1.61	0.87
1.57	7.79	1.62	1.03
1.30	7.82	1.61	1.25
1.05	7.80	1.62	1.53
1.36	7.81	1.62	1.19
1.36	7.81	1.62	1.19
0.42	7.83	1.62	3.88
1.57	7.83	1.62	1.03

TABLE TWENTY-ONE

Concentration of solution = 0.163
Grid leak = 5×10^8

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
0.78×10^{-6}	7.85×10^{-10}	1.62×10^{-12}	2.09×10^{-6}
0.48	7.87	1.63	3.39
0.47	7.90	1.64	3.48
0.94	7.89	1.63	1.73

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TABLE TWENTY-ONE (Con't.)

1.03×10^{-6}	7.89×10^{-10}	1.63×10^{-12}	1.59×10^{-6}
0.53	7.86	1.63	3.08
0.83	7.82	1.62	1.96
0.62	7.77	1.61	2.61
0.86	7.74	1.60	1.86
0.73	7.73	1.60	2.18
0.59	7.79	1.61	2.75
0.95	7.69	1.59	1.67
0.61	7.69	1.59	2.62
0.83	7.65	1.58	1.91
0.73	7.61	1.58	2.16

TABLE TWENTY-TWO

Concentration of solution = 0.152
Grid leak = 5×10^8

$\frac{\Delta S}{\Delta T}$	Current	Adsorption	Adsorption
($cm.^2/sec.$)	(amps.)	(gms./sec.)	(gms. $Hg_2^{++}/cm.^2$)
3.35×10^{-6}	8.27×10^{-10}	1.71×10^{-12}	0.51×10^{-6}
2.50	8.28	1.71	0.68
1.64	8.28	1.71	1.04
0.60	8.24	1.71	2.85
0.97	8.27	1.71	1.76
1.23	8.34	1.73	1.41
1.87	8.30	1.72	0.92
0.90	8.38	1.73	1.92
1.55	8.36	1.73	1.12
0.66	8.34	1.73	2.62
0.79	8.36	1.73	2.19
0.40	8.36	1.73	4.33
0.41	8.37	1.71	4.17
0.40	8.47	1.75	4.38
0.82	8.48	1.76	2.15
0.55	8.50	1.76	3.20
0.56	8.43	1.75	3.13
1.85	8.36	1.73	0.94
1.25	8.40	1.74	1.39
0.40	8.43	1.75	4.38

TABLE TWENTY-THREE

Concentration of solution = 0.143
Grid leak = 5×10^8

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
2.19×10^{-6}	8.75×10^{-10}	1.81×10^{-12}	0.83×10^{-6}
0.74	9.25	1.91	2.58
1.84	7.88	1.63	0.89
2.25	7.84	1.62	0.72
1.13	7.83	1.62	1.43
1.14	7.99	1.65	1.45
0.58	8.00	1.66	2.86
0.87	8.03	1.66	1.92
0.39	8.09	1.67	4.28
5.96	8.00	1.66	0.28
6.22	8.02	1.66	0.27

TABLE TWENTY-FOUR

Concentration of solution = 0.134
Grid leak = 5×10^8

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
2.39×10^{-6}	8.39×10^{-10}	1.74×10^{-12}	0.73×10^{-6}
1.63	8.27	1.71	1.05
1.68	8.19	1.70	1.01
0.59	8.27	1.71	2.90
0.53	8.53	1.77	3.34
5.67	8.46	1.75	0.31
0.92	8.75	1.81	1.97
3.51	8.31	1.72	0.49
2.79	8.31	1.72	0.62
2.85	8.31	1.72	0.60

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TABLE TWENTY-FOUR (Con't.)

2.89×10^{-6}	8.29×10^{-10}	1.72×10^{-12}	0.59×10^{-6}
3.49	8.29	1.72	0.49
2.06	8.29	1.72	0.83
2.47	8.31	1.72	0.70
3.67	8.21	1.70	0.46
2.95	8.17	1.69	0.57
2.99	8.16	1.69	0.57
4.42	8.15	1.69	0.38

TABLE TWENTY-FIVE

Concentration of solution = 0.048
Grid leak = 5×10^{8}

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
1.12×10^{-6}	1.50×10^{-10}	31.05×10^{-14}	0.28×10^{-6}
0.57	1.48	30.63	0.54
0.59	1.45	30.02	0.51
0.39	1.38	28.57	0.73
0.88	1.32	27.32	0.31
0.31	1.22	25.25	0.81
0.61	1.10	22.77	0.37
0.41	0.98	20.29	0.49
0.51	0.87	18.01	0.35
0.42	0.79	16.35	0.39
0.52	0.72	14.90	0.29
0.42	0.67	13.87	0.33
0.96	0.42	8.69	0.09
0.43	0.36	7.45	0.17
0.43	0.34	7.04	0.16
0.44	0.33	6.83	0.16
0.44	0.32	6.62	0.15
0.45	0.32	6.62	0.15
0.56	0.33	6.83	0.12
0.28	0.34	7.04	0.25
0.24	0.36	7.45	0.31
0.52	0.31	6.42	0.12
0.30	0.30	6.21	0.21

TABLE TWENTY-SIX

Concentration of solution = 0.018
Grid leak = 5×10^8

$\frac{\Delta S}{\Delta T}$ (cm.²/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++}/cm.²)
2.02×10^{-6}	2.82×10^{-12}	5.84×10^{-15}	2.89×10^{-9}
0.84	3.62	7.49	8.92
0.94	4.03	8.34	8.87
0.76	4.03	8.34	10.97
0.87	4.03	8.34	9.59
0.56	3.22	6.67	11.91

In the tables below are the figures for the runs made using the galvanometer alone, and the formula $\Delta S = 2\pi r \Delta h$. In the first column is given the concentration of solution in milli-mols of mercurous sulfate per liter; in the second is the rate of change of mercury surface in contact with the solution, found by the second method mentioned above under Measurement of Area Changes; in column three the current flowing between the electrodes is given in amperes; column four gives the adsorption per second, found as before; column five gives the adsorption in grams of mercurous ion per square centimeter of mercury surface.

Several runs were made at each concentration. Each horizontal line represents the mean of these runs.

TABLE TWENTY-SEVEN

Sensitivity of galvanometer = 4.43×10^{-10} amps. per mm.

Concentration of Hg_2SO_4 in milli-mols per liter	$\Delta S/\Delta T$ (cm.^{2}/sec.)	Current (amps.)	Adsorption (gms./sec.)	Adsorption (gms. Hg_2^{++} /cm.^{2})
1.12	4.21×10^{-6}	7.14×10^{-9}	14.78×10^{-12}	3.09×10^{-6}
0.95	3.45	4.01×10^{-8}	8.30×10^{-11}	2.41×10^{-5}
0.80	4.73	4.81	9.95	2.11
0.68	8.74	7.99	16.54	2.20
0.58	2.83	3.30	6.82	2.39
0.28	2.49	2.97	6.15	2.38
0.24	9.78	10.94	22.65	2.32
0.20	21.17	23.99	49.66	2.36
0.15	23.34	27.91	57.77	2.19
0.08	8.69	8.75	18.11	2.09
0.04	9.84	8.33	17.24	1.85
0.02	12.93	4.83	10.01	0.80
0.01	8.18	2.00	4.14	0.53

Also under this heading, EXPERIMENTAL RESULTS, the following facts should be pointed out:

(1) When a mercury surface was exposed to a solution of lead sulfate, no current was recorded. This experiment was tried in lead sulfate solutions of various concentrations in the same manner as that used for mercurous sulfate.

(2) It was noticed that as long as the rate of area change of the mercury drop was kept below the value of 2 or 3 $\times 10^{-5}$ cm.^{2} per second, the direction of the galvanometer deflection indicated that the mercury was positively charged. When the rate was increased to higher values, the direction of deflection was reversed.

Both the above facts support the idea of adsorptive rather than electrostatic forces causing the currents.

DISCUSSION OF EXPERIMENTAL RESULTS

An examination of Tables 2-26 immediately raises the question, how can such varying adsorptions be compared? The results were compared as shown in Figure Seven, A and B. In Figure Seven A is shown a plot of adsorption values against rates of change of mercury surface. All the points lie on a smooth curve, and it seems perfectly reasonable to assume that adsorption should vary in this way with rate of area change; that is, the faster the drop grows, the shorter the time allowed for the attempt of the adsorption process to attain equilibrium and the less the adsorption. At such low rates of area change, however, one asks why the adsorption equilibrium should not be established at all these rates below a certain limit. Since with the galvanometer method the results show that as long as the rate of area change is kept below 2 or 3 x 10^{-5} cm.^{2} per second the adsorption value changes but little, it must be supposed that the vacuum tube amplifier must be more sensitive to small area changes than is the galvanometer. This is not unreasonable.

It should also be noted that, while adsorption seems to vary greatly with variations in rate of change of surface, the current flowing between the electrodes varies only by small degrees. The following line of reasoning may be employed to account for this fact.

The potential difference across the two electrodes in the cell will be governed by the ratio of the mercurous ion concentrations at the two electrodes. That is

$$E = - \frac{RT}{NF} \ln \frac{c_1}{c_2}$$

This concentration ratio depends directly upon the rate at which the surface is increasing at low values of $\Delta S/\Delta T$. Therefore, if

$$\frac{c_1}{c_2} = K \frac{\Delta S}{\Delta T}$$

Then,

$$E = - \frac{RT}{NF} \ln K \frac{\Delta S}{\Delta T}$$

Also, if

$E = IR$ (the resistance of the circuit is constant)

Then,

$$I = \frac{T}{NF} \ln K \frac{\Delta S}{\Delta T}$$

With such an equation as this, an explanation is had at once as to why the current obtained should not vary greatly with changing rates of area change. To double this current, one must double the logarithm of $\Delta S/\Delta T$, which would mean a tremendous change in area-change rate. Such large differences in $\Delta S/\Delta T$ did not exist.

A plot of ln $\Delta S/\Delta T$ against Adsorption, then, should give a straight line. Such a graph is shown in Figure Seven B.

Figures Seven A and Seven B were drawn from the values given in Table Two. While plotting ln $\Delta S/\Delta T$ against adsorption does not completely straighten out the curve in Figure Seven A, it does give a much more nearly straight line. The slight curving of the line in Figure Seven B may be blamed on variations in current measurement due to slight drift of the vacuum tube circuit, overbalance, slow change of tube characteristics, and so forth. The broken line in Figure Seven B shows that a straight line could be drawn with reason between the points.

By similarly plotting the values given in each of the tables, 2 through 26, and taking the point at which the curve intersects the co-ordinate corresponding to $\Delta S/\Delta T = 1 \times 10^{-6}$ cm.^{2} per second as the adsorption at that rate of change of mercury surface, the adsorptions values at different concentrations were all referred to a common rate of change of mercury surface. For instance, in Figure Seven A, the adsorption

equals 1.54 x 10^{-8} gms. Hg_2^{++} at $\Delta S/\Delta T = 1 \times 10^{-6}$ cm.^{2} per second.

The adsorption values thus obtained were plotted against the Concentration of the Solution in milli-mols of mercurous sulfate per liter. These curves are shown in Figures Five and Six.

No claim is made that these are absolute values for the amount of mercurous ion adsorption. The only conclusions deduced from these data are that (1) above a certain concentration, in dilute solutions of mercurous sulfate, the amount of adsorption is constant, that (2) this so-called "critical concentration" is found to be about 0.08 milli-mols of mercurous sulfate per liter, and that (3) adsorption appears to be a function of the value of the grid leak.

The first conclusion is the same as that drawn from the works of Seidel, Shea, and Glidden who discuss the phenomenon in the papers mentioned in the Introduction.

The second conclusion recognizes a slightly lower value than given in previous works. Support for this value is gained by observing that the break in the curve comes at the same concentration in both the vacuum-tube and galvanometer methods.

The third conclusion is manifestly absurd. While the same general characteristics were shown by the curves with each of the three grid leaks, each curve was at a different height on the adsorption ordinate, its place being determined by the value of the grid leak. The lower the value of the grid leak, the higher became the value for adsorption. Since no relation should exist between the two factors, the only explanation that could be offered was the fact that, with the circuit as shown in Figure Four, part of the current flowing between the two electrodes, in being opposed by a resistance, much higher than the resistance of the solution in parallel with the solution, was not allowed to flow through the vacuum tube circuit, but was pushed to earth. This idea seems to be valid, because as the value of the grid leak became smaller and approached the resistance of the solution (about 8 x 10^{16} ohms from conductance measurements), the value of the amount of mercurous ion adsorbed climbed. Since even with a grid

leak as low as 10^6 ohms the tube circuit suffered a decided lowering of sensitivity and steadiness, it was decided to use a galvanometer connected directly to the adsorption cell in order to insure measurement of all the current flowing in the cell. It was thought that this latter course could be pursued safely with a galvanometer sensitive to 10^{-10} amperes per millimeter, since if a current of 10^{-12} amperes was flowing through the tube circuit with a grid leak of 10^8 ohms, this being only part of the total current, then the total current should certainly be large enough to be measurable on such a galvanometer.

The results of the runs made with the galvanometer are given in Table Twenty-Seven, and are plotted in Figure Eight.

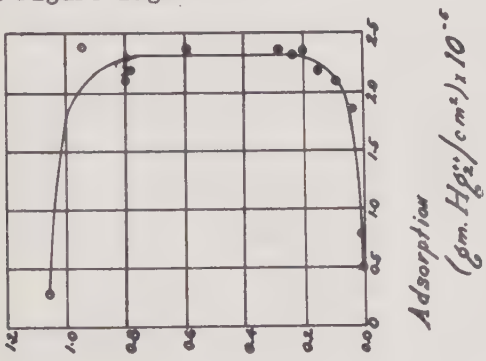

FIGURE 8

The value of the adsorption on the flat part of the curve is 2.34×10^{-5} gms. Hg_2^{++} per cm.^{2} This value is about twenty times higher than the values of Seidel and Shea and about sixty times higher than that obtained by Glidden. The same type of curve, however, was obtained for concentrations below 0.90 millimols of mercurous sulfate per liter. The break in the dilute range checks that of the vacuum tube curves. No attempt will be made to explain the break in the curve in the concentrated range at this time, since it is

believed that the phenomenon with which we are dealing either does not exist or is greatly altered at concentrations nearing saturation. The outstanding question to be answered is why the adsorption value should differ so markedly from those of previous experimenters.

With an adsorption value of

$$2.34 \times 10^{-5} \text{ gms. } Hg_2^{++} \text{ per cm.}^2,$$

$$\frac{2.34 \times 10^{-5}}{401.2} \times 6.06 \times 10^{23} = 3.53 \times 10^{-16} \text{ ions per cm.}^2$$

Considering close-packing of the mercurous ions in the film around the mercury drop, the area occupied by one mercurous ion is

$$(d^2) \times .866 = \text{area per ion} \quad (d = \text{diameter})$$

The reciprocal of this quantity gives the number of ions per cm.^{2} Four values from the X-ray data for the radius of the mercurous ion under different conditions (ranging from solid mercury to liquid mercury) were obtained. Substituting these values in the above formula we obtain,

If	Then
$r = 1.55 \times 10^{-8}$ cm.;	ions per cm.$^2 = .12 \times 10^{16}$
1.48	.13
1.10	.24
0.72	.60

At best, the agreement with our figure is poor. To account for the large discrepancy between our value and that of the gravimetric method, the following mechanism of adsorption is postulated.

Suppose, as seems very reasonable, a thin film of oxide surrounds the mercury surface. As the area of the drop is increased, mercurous ions from the solution displace the oxide film, enter the mercury surface and are discharged. A positive charge is thus built up on the drop (this is substantiated by the direction of galvanometer deflection). This accumulation of positive electricity attracts sulfate ions which

orient themselves around the drop. The layer of negative ions then causes more mercurous ions to arrange themselves in line with the sulfate ion layer. Now, as far as removal of mercurous ion from solution is concerned (meaning removal as far as possibility of analysis is concerned) we have taken out of solution both the discharged mercurous ions which have actually entered the Hg surface and the undischarged mercurous ions which are arrayed about the sulfate ions. We have put into solution the mercury which was originally present as mercurous oxide.

The analyst, then, measures the difference between the amounts of mercurous ion put into and taken from solution. The electrical method measures the mercurous ions discharged at the mercury surface. This, in itself, necessarily causes the gravimetric method to give a lower value for adsorption than that of the electrical method.

If

x = area of the O atom, then

$\frac{1}{x}$ = the number of O atoms per cm.^{2} in the postulated mercurous oxide layer.

Also, if

y = area of the sulfate ion, then

$\frac{1}{y}$ = no. of SO_4 ions per cm.^{2} oriented about the Hg surface.

Then the equations

(1) $\frac{2}{y} - \frac{1}{x} = a$, where a is the number of mercurous ions per cm.^{2} by the gravimetric method, and

(2) $\frac{1}{y} = b$, where b is the number of mercurous ions per cm.^{2} by the electrical method,

should give a fairly definite mathematical interpretation of the quantities measured in each case.

From these equations

$$y = \frac{2x}{ax + 1}$$

If values calculated from X-ray measurements be substituted for x and y, then

$$24.97 \times 10^{-16} = \frac{2 \times 8.32 \times 10^{-16} \times 401.2}{1.1 \times 10^{-6} \times 6.06 \times 10^{23} \times 8.32 \times 10^{-16} + 401.2}$$

$$24.97 \times 10^{-16} = 6.99 \times 10^{-16}$$

Since, however, the structure of the sulfate ion compels those ions to settle upon the close-packed mercurous ions so that there is only one sulfate ion for three mercurous ions, the right side of the above equation should be multiplied by three. That is,

$$24.97 \times 10^{-16} = 20.97 \times 10^{-16}$$

This agreement is good.

If, however, the two equations (1) and (2) are solved simultaneously to give

$$x = \frac{1}{2b - a}$$

introducing adsorption values from both methods gives

$$8.32 \times 10^{-16} = \frac{401.2}{2 \times 2.34 \times 10^{-5} \times 6.06 \times 10^{23} - 1.1 \times 10^{-6} \times 6.06 \times 10^{23}}$$

$$8.32 \times 10^{-16} = .15 \times 10^{-16}$$

Or, if the equation

$$\frac{1}{y} = b \quad \text{is used,}$$

$$\frac{2.34 \times 10^{-5} \times 6.06 \times 10^{23} \times 24.97 \times 10^{-16}}{401.2} = 1$$

$$88.2 = 1$$

as before, taking one-third the area of the sulfate ion,

$$29.4 = 1$$

The agreement with X-ray measurements, as shown in the figures on page 39 and on the preceding page, is none too good if the adsorption value from the electrical method is used, but is fairly good if the adsorption value from the gravimetric method is used. It seems, then, since the same mechanism is used to explain the measurements by both methods, that such a mechanism at least approaches the true picture. Some variable, as yet unaccounted for, must enter into the measurements by the electrical method; this variable, however, should not destroy the validity of the postulation of the adsorption mechanism made here, but, when discovered, should reconcile the two methods.

Momentarily, disregarding the disagreement of the values as shown above, let us point out two facts. Great care in experimental technique assures us that all the current flowing between the mercury electrodes is measured by the galvanometer, even though it still remains to account for part of this current. It is not unreasonable to believe that absolute adsorption values can be obtained by this method as more work is done.

The second fact for emphasis, and strong emphasis, is that no lead ions are adsorbed from a lead sulfate solution by a mercury surface. Heretofore, all work done on this subject hinged upon the fundamental assumption that specific adsorptive forces were being dealt with. It is safe to say, now, that this assumption is correct. The argument may be presented that even a saturated solution of lead sulfate would fall on the dilute end of the concentration-adsorption curve, where even the adsorption value on mercurous ion is low. However, expressing the concentration of lead sulfate solution in milli-mols per liter, the abscissa would fall at just about the point where the curve for mercurous sulfate begins to break, and where the adsorption value for mercurous ion is still about 2×10^{-5} gms. Hg_2^{++} /cm.^{2}. Moreover, absolutely no measurable quantity of adsorption is shown for the lead ion.

SUMMARY

1. Above a concentration of 0.08 milli-mols of mercurous sulfate per liter of solution, the adsorption of mercurous ion by mercury, by this method, is 2.34×10^{-5} gms. per cm.^{2}. The above value is constant from a concentration of 0.08 milli-mols per liter to a concentration of 0.90 milli-mols per liter.

2. The forces dealt with are specific adsorptive forces, and not purely electrostatic forces.

3. A certain time is required for attainment of the adsorption equilibrium, the adsorption varying linearly with the natural logarithm of the rate of change of mercury surface when this rate of change exceeds 2 or 3×10^{-5} cm.^{2} per second.

4. A mechanism for the adsorption process has been presented; this postulated mechanism seems to point to a reconciliation between the electrical and gravimetric methods of analysis of this particular type of adsorption.

5. The use of a sensitive galvanometer for measurements of this type is more practical than the use of a very sensitive amplifier of the FP-54 Pliotron type.

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BIOGRAPHY

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